# PATENT SPECIFICATION

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COMPLETE SPECIFICATION

## A Process for the Production of Silver-containing Layers on Aluminium and its Alloys

We, Dr. VON GLUTZ & MÜLLER AKTIENGESELLSCHAFT, of Sonnenbergstrasse 26, Baden, Switzerland, a Swiss Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

By a known process for producing representations and reproductions of all kinds with the aid of photo-sensitive substances, the absorbent, oxidic layer, such as is produced by anodic oxidation on aluminium, can be used as the sole carrier for the photo-sensitive substances. In this connection, the presumption is that the photo-sensitive substances are located in the pores of the anodic film of oxide but, in no case, on the surface of the layer. Hitherto, essentially two processes have been proposed and employed for sensitising the anodic film to light. By one process, the porous layer is impregnated with a solution of a substance that is already photo-sensitive, for example a ferric salt, and, by the other process, the photo sensitive substance, for example a silver halide, is produced by double decomposition of the film itself. If one dispenses with the very limited employment of oxide layers sensitised with iron salts, only the films sensitised with silver halides remain for a wider basis of employment. The process, hitherto usual, of double chemical decomposition by means of precipitation reactions, for example with silver nitrate and potassium bromide, has, however, very considerable disadvantages. Thus, in order to incorporate sufficient silver halide, it is necessary to repeat the precipitation reaction a number of times. However, even this would not, in the case of the ordinary anodic films, for example in the case of films produced with direct current in sulphuric-acid solution, lead to the object aimed at, since volume of their pores would be far too small. A special process must, therefore, be employed to obtain films with the necessary absorptive power. For this purpose, a few processes have already ben proposed, for example the direct-current anodisation in warm chromic-acid solution or in chromic-acid solutions with a varying content of sulphuric acid, or the successive treatment in a chromic-acid solution and an oxalic-acid solution; it has also been attempted to render the ordinary anodic layer more absorbent before sensitising by chemical means or by thermal treatment. Phosphate and fluoride layers have also been proposed as carriers for the photo-sensitive substances. All these expedients lead to layers which do not approach ordinary layers with regard to hardness, resistance to wear, closability of the pores by sealing surface smoothness and resistance to corrosion. It has also been found that, in the precipitation reactions, the photo-sensitive products are principally deposited at the open ends of the pores—a phenomenon which can be explained by the laws of diffusion and osmosis.

All that has hereinbefore been stated applies not only to the production of photo-sensitive layers but to all cases in which it is desired to provide the film with metallic or combined silver in sufficient quantity, whether it be merely for decorative purposes, for example colouring, or as an adhesive base for galvanic covering layers.

According to the present invention, by means of which the disadvantages hereinbefore mentioned are obviated, there is used, for the purpose of producing silver-containing layers on aluminium and its alloys, a process which is characterised by the feature that there is first produced, on the light metals mentioned, an absorbent, firmly adhering, oxide layer, a dyestuff

which reduces silver compounds to metallic silver is deposited in the pores in this layer and, finally, metallic silver is precipitated in the pores in this layer by chemical reaction by means of a solution that contains silver.

It has been found that a large number of organic compounds which are capable of reducing silver ions, can easily be deposited in the oxide layer down to the bottom of the pores, either in the form of more or less concentrated solutions in water or other solvents by simple impregnation or by actual "going on" by chemical or physical actions, for example by diffusion and adsorption from solutions, similarly to the dyeing of textiles by coal-tar dye-stuffs.

There are a large number of organic compounds, especially those having the character of a dyestuff, which dye the oxide layer fast, similarly to the dyeing of wool and cellulose by textile dyestuffs. Among these, there have been found to be specially advantageous, for the process according to the invention, dyestuffs having the character of mordants, i.e., dyestuffs which have a certain chemical affinity to aluminium oxide, for example derivatives of anthraquinone (alizarin types), of flavone and xanthone, or derivatives of pronin (gallein type) and oxazine (gallocyanin type). The colour of these compounds plays no part but the compounds only meet the requirements that they should go fast on to the aluminium-oxide layer and that they should be able to reduce the silver ions to metallic silver. The expression "go on" or "going on" used herein relates to the phenomenon in which a material, for example the oxide coating, extracts the dyestuff from a solution thereof and absorbs it in itself. There are, for example, derivatives of gallic acid which are not coloured but which can, however, go on to the aluminium oxide. A principal condition, which as to be fulfilled by the organic compounds in the sense of the invention is that they reduce the silver compounds to metallic silver. It has been found that, in most cases, this condition is fulfilled when at least two hydroxy or amino groups are in the ortho or para position to each other in the ring system or when a reactive aldehyde group is contained in the molecule.

The following are mentioned as examples of suitable dyestuffs: 1:2:5:8-tetrahydroxyanthraquinone, 1:5-dihydroxy-4:8-diaminoanthraquinone-2-sulphonic acid, 3:5:7:3:4¹-pentahydroxy-flavone (quercitin), dihydroxy-fluorescein (gallein) and gallocyanin.

Numerous dyestuffs, chiefly derivatives of benzene or naphthalene, which have hydroxy or amino groups in the ortho or para position, are suitable for impregnating the abosrbent, firmly adhering layer with more or less concentrated solutions in water or other solvents. It is especially advantageous to select compounds which are soluble in organic solvents but not in cold water such as, for example, 4-nitro-2-amino-1-phenol, 6-nitro-2-amino-phenol-4-sulphonic acid, 4:6-dintro-2-amino-phenol, *p*-hydroxyphenylglycin, methyl-*p*-aminophenyl, ethyl galate gallicanilide.

The absorbent, firmly adhering oxide layer may be produced on the aluminium and its aloys in many ways. Thus, useful layers may be obtained by known methods by immersion in, for the most part, warm chemical reaction solutions. Such solutions may have an alkaline or acid reaction; they contain certain substances which favour the formation of the oxide layer, for example, chromates, complex fluorides, silicofluorides, phosphates, ferricyanides, vanadates, molybdates and similar substances. Suitable layers can also be obtained by treating the aluminium in molten mixtures of salts with an oxidising action.

It may also be advantageous to employ the known processes of anodic-electrolytic oxidation of aluminium and its alloys for the purpose of producing an absorbent, firmly adhering, oxide layer. These processes are all characterised by the feature that the aluminium article is connected as anode in mostly acid baths and electrolysis is carried out for a definite time by means of direct or alternating current. The anodic oxide layers have the advantage of being especially hard and resistant to mechanical and chemicl strain, of being easily dyed by coal-tar dyestuffs and of being given a glass-hard, unsoilable surface property by suitable port-closing processes.

It has been ascertained by experiments that, for certain purposes, not all anodically producible layers are equivalent. If, for example, the process is to be employed for the production of photographic copies on aluminium or aluminium alloys, the layers must withstand a series of treatments without altering unfavourably. It is necessary that a good absorptive power and photographic capacity, as well as unchangeability should be maintained during the time taken by the treatment. It has been found that, for photographic purposes, suitable layers, which may be employed with great advantage as carriers for the silver-containing substance, are absorbent, firmly adhering, oxide layers which have been produced anodically with

the aid of direct current in an aqueous solution which contains free oxalic acid as well as soluble oxalates and has a *p*H value between 1.2 and 4.0. Suitable soluble oxalates are those of alkali metals and also those of metals of the titanium group, i.e., titanium, zirconium and thorium. With the former oxalates, clear, colourless, transparent layers are obtained, whilst with the latter oxalates non-transparent, opaque layers are obtained. The advantages of the employment of these layers for the purposes of the present invention are considerable. In addition to a good hardness and resistance to abrasion, they possess a high chemical resistance; they are very porous and absorbent and can very easily be dyed. On closing the pores by means of the usual warm, aqueous solutions, their surface becomes glass-hard and unsoilable.

The reaction of the dyestuff, deposited in the layer, with solutions containing silver in the form of ions is advantageously carried out by immersing the suitably pre-treated article in the reactive silver solution; the latter may have a slightly acid, a neutral or a slightly alkaline reaction according to the reactivity of the dyestuff. Ammoniacal silver solutions, preferably those having no or only a slight excess of ammonia, have been found to be advantageous and usable in most cases. The temperature of and the time taken by this immersion treatment depend upon the nature of the layer and upon the kind of dyestuff. Advantageously, the dyestuff selected is a substance the oxidation products of which can be dissolved out without trouble from the absorbent layer on the reduction of the silver salt, so that none of them remain behind in the layer.

By the process according to the invention it is possible to precipitate metallic silver in sufficient quantity down to the base of the pores in the oxide layers. The appearance of the layer can be selected at will within wide limits from light brown, through darker stages of brown and satin-like black to a mirror with a metallic lustre.

If it is desired to use the layer in this form as the final stage, this will, as a rule, be followed by a treatment by which the pores are closed. This may be carried out in the usual manner, as by depositing fatty substances or varnishes or by immersion in warm solutions of hydrolysing salts, for example nickel and cobalt salts, or in boiling water or by treatment with steam.

The silver-containing layers obtained by the process according to the invention may be subjected to other treatments instead of or before the closing of the pores. The metallic silver precipitated in the layer is present in an ultramicroscopically fine state. It can readily be re-oxidised to a silver compound. Thus, according to the present invention, it is easily possible to convert the metallic silver into a photo-sensitive silver halide by immersing the article provided with the silver-containing layer either in a solution containing at least one oxidising agent and one or more halides or by exposing it to a damp atmosphere which contains at least one halogen element (e.g. chlorine gas). If silver chloride has been produced in this way, it can be converted wholly or partially into the corresponding bromide or iodide by treatment with solutions of bromides or iodides. In this way, it is possible to vary the degree of photo-sensitivity in wide limits. Such prepared articles, for example sheets of metal, can also be employed for photographic purposes in a similar manner as photographic plates on glass or as prepared films or papers. They may be exposed beneath a suitable photographic negative and developed in a suitable mineral or organic developer; the pictures produced may be toned, intensified, reduced and fixed in the known manner after finishing the drawn or photographic representation, i.e., by colouring it or sealing it or by intensifying the silver image to produce relief by galvanic plating.

The process according to the invention may advantageously be used for producing firmly adhering coatings on aluminium and aluminium alloys. The layer containing metallic silver conducts electric current on the surface, so that, by cathodic connection of the aluminium article, the oxide-silver surface can be directly silvered, copper-plated, nickel-plated, or chromium-plated in the known galvanic baths. For this purpose, it is advantageous to rinse, for a short time, the article leaving the silver solution and then to put it dripping wet into the galvanic bath.

The process according to the invention can also be employed for the production of printing products such as, for example, sign-boards, scales, drawings, inscriptions and autotypes. The layers, produced according to the invention and containing metallic silver, are coated at the places that are to remain unaltered, with a resist paste which is resistant to nitric acid and other silver-dissolving agents, and the silver is then dissolved out at the uncoated places. After the sealing or removal of the resist paste, polishing and

cutting, the products are finished. The reverse procedure may also be followed to arrive at the same result. The absorbent, firmly adhering, oxide layer is printed with resist paste at the places that remain white, a dyestuff which reduces silver compounds to metallic silver is allowed to go on in the layer at the places that remain free and the whole is reacted with the silver solution and metallic silver is formed. The printing process first hereinbefore mentioned is better suited to the case in which it is desired to colour the places that have been freed from silver or to print them repeatedly with employment of a resist, so that multicoloured printing products can be obtained.

A further possibility of producing pictorial, drawn or written representations of all kinds with the aid of the present invention for the purpose of the production of sign-boards, scales, maps and other printing products and photographic reproductions consists in that the dyestuff, which reduces the silver ions to metallic silver, is deposited in the absorbent, firmly adhering, oxide layer in the desired pictorial representation before it is brought into reaction with the silver solution. It has been found that, for the purpose of achieving this object, various ways may be adopted in the scope of the present invention. For example, the dyestuff, which reduces the silver ions to metallic silver, is deposited in the layer before or after the coating with resist paste. In the former case, the positive picture is produced with employment of a resist and the dyestuff is again dissolved out at the places which have remained free. In the second case, the absorbent layer is printed as a negative with the resist paste and the dyestuff is deposited only subsequently. A further embodiment of the process consists in selecting a dyestuff which reduces the silver compounds to metallic silver and which, under the influence of light, is altered in such a manner that, after the exposure, it can be separated from its exposure product either chemically or physically. For example, a suitable diazonium compound, for example 1-diazo-2-naphthol-4-sulphonic acid may be deposited in the absorbent layer. After exposure beneath a negative or a positive, the insoluble azo dyestuff can be produced in the layer at the places unaffected by the light by soaking in a suitable solution, for example in a slightly alkaline solution of polyhydroxybenzene, and, finally, the silver image can be produced after the soaking. It has been found that, by this process, the production of incombustible copies of documents is possible in an economical manner.

The layer, which contains metallic silver and which is produced according to the invention, can, as long as it is not sealed, be further altered by bringing the precipitated or occluded silver into contact with substances which can react with it for the purpose of altering the colour shade or the appearance. Thus, reddish to purple-brown shades can be obtained with solutions of copper sulphate, potassium citrate and potassium ferricyanide, sepia-like shades can be obtained with solutions of uranium nitrate and potassium ferricyanide, and blue shades can be obtained with solutions of potassium ferricyanide and ferric citrate. Further, the silver in the layer can, by treatment with solutions of gold salts or platinum salts, be replaced by the nobler metal.

### Example 1

A pure aluminium foil, with an aluminium content of 99.6% and a thickness of 0.05 mm., is provided with a firmly adhering, absorbent, oxide layer by immersing it for five minutes in a hot solution of 25 gms. of sodium carbonate and 15 gms. of potassium ferricyanide. After rinsing and drying, the oxidic layer produced is impregnated with a 10% solution of 4-nitro-2-amino-1-phenol in alcohol, allowed to drain and dry and the yellow-coloured layer is then immersed in a 1% solution of silver nitrate at 60° C., to which some ammonia has been added. A brown coloration is produced. Finally, it is thoroughly rinsed and dried. The aluminium foil prepared in this manner is very suitable for the sterile treatment of wounds or for the self-sterile covering of open wounds or serious injuries to the skin.

### Example 2

A solution of 3000 gms. of potassium oxalate in 100 litres of water is prepared. Oxalic acid is then dissolved therein until the solution has a *p*H value of 2.8. In the solution, heated to 55° C., an aluminium sheet is treated, with movement of the liquid, anodically with a current density of 2.0 amperes per square decimetre with direct current. The layer produced is as clear as glass and colourless. The aluminium sheet is then rinsed with water for a short time and is immersed for 15 minutes in a solution of the azo dyestuff at 60° C. which is produced from diazotised 5-amino-salicylic acid and resorcinol. The dyestuff goes on in the layer with a red colour. After rinsing in water, the sheet coloured in this manner is immersed for one hour in a solution at 45° C. which contains 10

gms. of silver nitrate in 1 litre of water and as much ammonia as is just necessary for the formation of silver-ammonia nitrate. A black coloration having an excellent fastness to light and weather is produced. By converting the metallic silver into silver halide, a photographic material for copying purposes is obtained.

EXAMPLE 3

A sheet of pure aluminium is anodically treated with a current density of 2 amperes per square decimetre in the following solution at 58° C. with direct current for 35 minutes. The solution is produced by dissolving 2000 gms. of the double salt titanium-potassium oxalate in 100 litres of water and adding oxalic acid until the solution has a *p*H value of 2.1. The layer obtained in this way is non-transparent and of a whitish light grey. Instead of the sheet, finished shaped articles or parts thereof or pieces produced from profiles may be employed. After rinsing, the sheet etc. is treated in a solution at 60° C. of 20 gms. of 1:5-dihydroxy-4:8-diaminoanthraquinone-2:6-disulphonic acid in 1 litre of water until a deep blue coloration, which is fast to water, is produced. The sheet is then allowed to react with a solution of 25 gms. of silver-ammonia nitrate in 1 litre of water at 45° C. for 3 hours, the colour changing from blue into a deep black. The object is now immersed in a solution of 10 gms. of sulphuric acid, 2 gms. of potassium permanganate and 15 gms. of sodium chloride in 1 litre of water until it has become white. This treatment is carried out in red light. After thoroughly rinsing in water and after drying, the sheet is exposed beneath a transparent photographic negative, developed in a photographic developer, toned in a gold toning bath, fixed and rinsed. Finally, for the purpose of closing the pores, it is after-treated in a hot solution of a nickel salt or in boiling water. A photographic copy of a clear effect which is rich in contrasts is produced.

EXAMPLE 4

A sheet of pure aluminium 0.25 mm. thick is anodised for 35 minutes in an aqueous solution, free from sulphuric acid of 6% of chromic acid and 1% of titanium potassium oxalate at 60° C. with a current density of 1 ampere per square decimetre. The whitish oxide layer produced is then dyed deep violet in a 1% solution of dihydroxyfluorescein (gallein). By reacting the dyestuff in a solution of 20 gms. per litre of silver-ammonia nitrate, a deep black coloration is produced by the occluded, finely divided metallic silver. The sheet is then exposed, in a closed vessel at dark-room illumination or in the dark, to the action of a damp atmosphere containing elementary chlorine gas. In this way, the silver is oxidised to silver chloride. As soon as all the silver has been converted, as can easily be ascertained by the whitish colour, the sheet is first rinsed with a very dilute solution of sodium carbonate and then with clean water and allowed to dry. The sheet prepared in this way is excellently suitable, especially in conjunction with an acid, so-called physical developer, for the production of black-and-white reproductions, for example for the photographic reproduction of cards and incombustible documents or for the production of sign-boards and absolutely correct scales and rules.

EXAMPLE 5

A sheet of a thermally compensated aluminium alloy of the Al-Mg-Si type is anodised for 30 minutes in a solution, at 20° C., which contains 12% by weight of sulphuric acid and 5% of oxalic-acid hydrate, with direct current at a current density of 2 amperes per square decimetre and is then dyed to a deep red colour in a 2% solution of 1:2:4-trihydroxyanthraquinone. By immersing in a solution at 60° C. containing 20 gms. of silver-ammonia nitrate per litre of water, a deep black precipitate of metallic silver is produced which replaces the dyestuff that has gone on. After rinsing and drying, the sheet is printed in any desired pattern with an oily printing ink by means of which a resist is applied to the places that then remain black. By immersing the printed sheet in a 30% solution of nitric acid, the metallic silver is dissolved out at the unprinted places and the appearance of the original anodic layer is restored. After boiling the sheet in water and after removing the resist printing ink, the printed product is finished. In this way there are obtained sign-boards, drawn reproductions and inscriptions of great clarity and excellent fastness to light and weather.

EXAMPLE 6

An article made of an aluminium alloy of the Al-Zn-Mg type is anodised for 20 minutes in a 20% solution of sulphuric acid by means of direct current with a current density of 1.3 amperes per square decimetre and is then dyed, by immersion in a solution at 60° C. of 15 gms. of the known vegetable dye stuff Brasilin per 1 litre of water, to a deep red that is fast to water. After rinsing in water, the red dyestuff, that has gone on, is replaced by metallic silver in a warm

solution of silver-ammonia nitrate. After rinsing in water, the article is copper-plated for 45 minutes in a cold solution, which contains 170 gms. of copper sulphate, 60 gms. of sulphuric acid, 45 gms. of glycerine and 0.1 gm. of gelatine, with a current density of 1 ampere per square decimetre. The article, thus copper-plated galvanically, can now be used directly in this form. However, it can also be further coated galvanically with other metals or re-dyed to old bronze shades or green old copper by chemical treatment.

The Examples given represent a few possible methods of applying and carrying out the subject matter of the invention and the scope of the invention is not limited by them.

What we claim is:—

1. A process for producing silver-containing layers on aluminium or aluminium alloys, characterised by the feature that an absorbent, firmly adhering, oxide layer is produced on aluminium or aluminium alloys, a dyestuff which reduces silver compounds to metallic silver is deposited in the pores in this layer and, finally, metallic silver is precipitated in the pores in this layer by chemical reaction by means of a solution that contains silver.

2. A process according to Claim 1, characterised by the feature that the absorbent, firmly adhering, oxide layer is produced by chemical treatment of the aluminium or aluminium alloy in suitable media.

3. A process according to Claim 1, characterised by the feature that the absorbent, firmly adhering oxide layer is produced by anodic-electrolytic treatment of the aluminium or aluminium alloy in electrolyte solutions.

4. A process according to Claim 1, characterised by the feature that the absorbent, firmly adhering oxide layer is produced by anodic-electrolytic treatment with direct current in an aqueous solution which contains free oxalic acid and, at least one alkali oxalate and has a $p_H$ value between 1.2 and 4.0.

5. A process according to Claim 1, characterised by the feature that the absorbent, firmly adhering oxide layer is produced by anodic-electrolytic treatment with direct current in an aqueous solution which contains free oxalic acid and at least one oxalate of the titanium group and has a $p_H$ value between 1.2 and 4.0.

6. A process according to Claim 1, characterised by the feature that the deposition of the dyestuff as a reducing agent is effected by impregnating the oxide layer with a solution of the dyestuff.

7. A process according to Claim 1, characterised by the feature that the deposition of the dyestuff as a reducing agent is effected by the going-on of a dyestuff which possesses an affinity for the oxide layer.

8. A process according to Claim 1, characterised by the feature that the dyestuff consists of at least one compound which is of a mordanting character.

9. A process according to Claim 1, characterised by the feature that the silver-compound containing solution consists of an ammoniacal-silver solution.

10. A process according to Claim 1, characterised by the feature that the oxide layer which contains metallic silver is coated with metallic covering layers by galvanic treatment.

11. A process according to Claim 1, characterised by the feature that, for the purpose of producing representations of all kinds, the silver precipitated in the pores of the oxide layer is again dissolved out in places.

12. A process according to Claim 1, characterised by the feature that, for the purpose of producing pictorial and documentary representations of all kinds, parts of the oxide layer are covered with resist before their treatment with the dyestuff, so that, after the chemical reaction, only the uncovered places contain metallic silver.

13. A process according to Claim 1, characterised by the feature that, for the purpose of producing documentary, drawn, written and pictorial representations, the dyestuff is deposited in the absorbent, firmly adhering oxide layer only in places and in accordance with the desired representation.

14. A process according to Claim 1, characterised by the feature that the silver precipitated in the pores of the oxide layer is reacted with chemical substances for the purpose of altering the shade.

15. A process for producing silver-containing layers on aluminium or aluminium alloys, substantially as hereinbefore described in the Examples given.

16. Articles of aluminium or aluminium alloys, which articles have been treated by the process according to any of the preceding claims.

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